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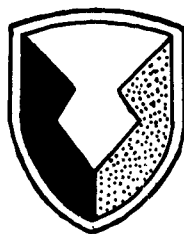
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COATING and CHEMICAL LABORATORY

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CCL REPORT NO. 141

IDENTIFICATION AND DETERMINATION OF PLASTICIZERS IN LACQUERS
BY PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

BY

GEORGE G. ESPOSITO

AMCMS CODE NO. 5026.11.84205
DA PROJECT I-H-0-24401-A-110-05

16 APRIL 1963

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Coating and Chemical Laboratory
Aberdeen Proving Ground
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ABSTRACT

Plasticizers are important modifiers of synthetic resins and their presence will greatly influence the physical characteristics of lacquers. This report describes a procedure for the identification and determination of seven plasticizers in nitrocellulose, vinyl and acrylic type lacquers by programmed temperature gas-liquid chromatography (PTGLC).

The chromatographic analysis is conducted on the sample which has been treated to remove the resins. Plasticizers are identified from their relative retention times and determined by the internal standard technique. The method is simple, rapid and accurate.

1. INTRODUCTION

Analytical methods have been developed for various components of lacquers but none have been adequately presented for the analysis of their plasticizer content. Plasticizers are usually present in the 5 - 15% range and represent an important part of a lacquer. The proper selection of plasticizer is essential in formulating a durable lacquer and will effect such characteristics as impact resistance, gloss, leveling, flexibility, flow, etc. There are a large number of plasticizers available, but in practice only a limited quantity are encountered. Several Military and Federal Specifications for nitrocellulose type lacquers have been issued which contain minimum and maximum requirements for plasticizer content. The volatility of plasticizers vary over a broad range and some tend to distil out of an aged lacquer film. No suitable method could be found for quality control purposes.

A gas chromatographic method (1) for the assay of butyl benzyl phthalate has been found in the literature. A method (2) for the identification of plasticizers in plastics by gas chromatography has been reported in which a variety of plasticizers were identified on two Apiezon K columns isothermally, but some peaks were exceptionally broad and asymmetric. Quantitative data was brief, not substantiated by knowns, and not related to the whole material.

The method described in this report utilizes a programmed temperature gas chromatographic procedure for the identification and determination of the plasticizers frequently encountered in lacquers. The peaks are narrow, symmetrical and congruous for quantitative use. Nitrocellulose, vinyl and acrylic lacquers of known compositions were prepared containing various phthalate plasticizers and tricresyl phosphate and good agreement between analytical and known values were obtained. A high temperature gas chromatograph unit capable of analyzing high boiling materials was employed in this study, but polymeric type plasticizers are not sufficiently volatile and cannot be determined by this method.

Chemical methods normally used for the identification of plasticizers are time consuming and in many cases inconclusive. Only limited quantitative data, such as, total phthalate and phosphate can be ascertained by chemical methods; and it is not possible to differentiate chemically between phthalate plasticizers and phthalate resins. The chromatographic analysis described in this report provide a rapid method for separating and determining individual plasticizers in lacquers including types very similar in chemical structure and permits the determination of phthalate plasticizers independently of phthalate resins, so that a correction can be made in subsequent chemical analysis.

The instrument is calibrated using known plasticizers with an internal standard and relative retention times and correction factors are obtained. A preliminary physical separation of plasticizer from resin is carried out by adding carbon tetrachloride and petroleum ether dropwise to an acetone thinned sample containing a weighed amount of internal standard. A portion of the solvent is evaporated and the plasticizers separated by PTGLC on a 6 foot silicone grease column.

II. DETAILS OF TEST

Chromatographic Unit

The equipment used to obtain the chromatograms was a Model 500 Linear Programmed Temperature Gas Chromatograph (F&M Scientific Co.) equipped with a Brown Elektronik recorder (Minneapolis-Honeywell) and a DiscIntegrator (Disc Instruments, Inc.).

Operating Conditions

Detector cell temperature, °C.	300
Detector cell current, ma.	160
Injection port temperature, °C.	330
Helium flow at exit, cc./minute	120
Programmed temperature details	
Column heating rate, °C./minute	4
Starting column temperature, °C.	210
Finishing column temperature, °C.	290

A 6-foot length of $\frac{1}{8}$ -inch copper tubing was packed with 20% by weight of silicone grease on acid and alkali washed chromosorb W.

Experimental

Weigh accurately about 100 mg. of internal standard (butyl adipate or butyl sebacate) into a 25 ml. flask followed by 2 - 3 grams of lacquer which is also accurately weighed. Add 1 ml. of acetone and insert a small magnetic stirring bar. While stirring rapidly, add 3 ml. of carbon tetrachloride dropwise (80 - 100 drops per minute). Continue stirring and add 3 ml. of petroleum ether in the same manner. Filter through rapid filter paper into a 25 ml. beaker, add a Berl saddle and place in a 70°C. water bath. Remove as soon as boiling subsides.

Heat chromatographic column to 210°C., set attenuation at point of low sensitivity and inject 10 - 20 μ l of sample onto the column. Immediately engage temperature programming mechanism. After solvents emerge, reset sensitivity according to type and amount of plasticizer present. When maximum temperature is reached, hold until chromatogram has completely developed.

The plasticizers are identified by calculating their retention times, relative to butyl sebacate, and comparing them to the calibration chart shown in Table I. The detector response is a function of molecular weight and structure, and response correction factors are obtained by chromatographing known weights of each plasticizers with the internal standard. The area of each peak is measured, corrected for detector response and the plasticizer determined from the known concentration of internal standard that has been added.

Results

The separation of plasticizers is illustrated in Figure 1. All plasticizers produced essentially one peak except tricresyl phosphate. Figures 2 and 3 shows the analysis of nitrocellulose lacquers containing phthalate

plasticizers. The lacquer shown in Figure 3 contains two plasticizers, diethyl phthalate and dibutyl phthalate, which can be determined in one analysis. All nitrocellulose lacquers examined produced a tailing peak in the first few minutes of operation and the pen had to be brought back to zero manually.

Figure 4 shows the analysis of an acrylic type lacquer plasticized with butyl benzyl phthalate. A vinyl-chloride lacquer containing tricresyl phosphate produced the chromatogram shown in Figure 5.

Quantitative data was obtained on known lacquers prepared from nitrocellulose, acrylic and vinyl resins plasticized with diethyl phthalate, dibutyl phthalate, di-(2-ethylhexyl) phthalate, butyl benzyl phthalate and tricresyl phosphate. The tabulated results are shown in Table II. Changes in attenuation are not noted on the chromatograms but are taken into consideration in the calculation.

III. DISCUSSION

It is inconceivable that a complete separation of all plasticizers is possible and there are certain to be combinations which cannot be resolved. The object of this investigation was to provide a method which would be suitable for the plasticizers most frequently encountered in lacquer coatings, and this is possible using the silicone grease column described. Additional information can be obtained on a polar, 6-inch 20% polyester column which affects the order of elution of some plasticizers.

Both dibutyl sebecate and dibutyl adipate were used as internal standards in this study. Dibutyl sebecate is preferred for establishing relative retention times and for quantitative work because of the position it occupies on the chromatograms. Dibutyl adipate is available in higher purity and was used for the butyl benzyl phthalate analysis because a small amount of impurity in butyl sebecate caused some interference. The butyl benzyl phthalate used to prepare the known contained 5% dibutyl phthalate and no detectable amount of dibenzyl phthalate. If the determination of dibenzyl phthalate is desired it is best to repeat the analysis isothermally at 180°C.

The procedure described in this report is applicable to single plasticizers or mixtures and provides a better insight into the composition of unknown lacquers received for examination. The utilization of PTGLC makes available a scheme suitable for a broad range of plasticizers producing narrow symmetrical peaks in a reasonable length of time.

IV. REFERENCES

1. Cook, C. D., Elgood, E. J., Shaw, G. C., and Solomon, D. H., Anal. Chem., 34, 1177 (1962).
2. Lewis, J. S. and Patton, H. W., in "Gas Chromatography", V. J. Coates, H. J. Noebels, and I. S. Fagerson, eds., p. 145, Academic Press, New York, 1958.

APPENDIX A

Tables

TABLE I

RELATIVE RETENTION TIME DATA FOR PLASTICIZERS

	Relative Retention Time (Dibutyl sebecate = 1)
Dimethyl phthalate	0.16
Diethyl phthalate	0.26
Dibutyl phthalate	0.67
Butyl benzyl phthalate	1.32
Di-(2-ethylhexyl) phthalate (DOP)	1.65
Tricresyl phosphate	1.78 - 1.97*
Diethyl sebecate	2.20

* Produces several peaks in this range.

TABLE II

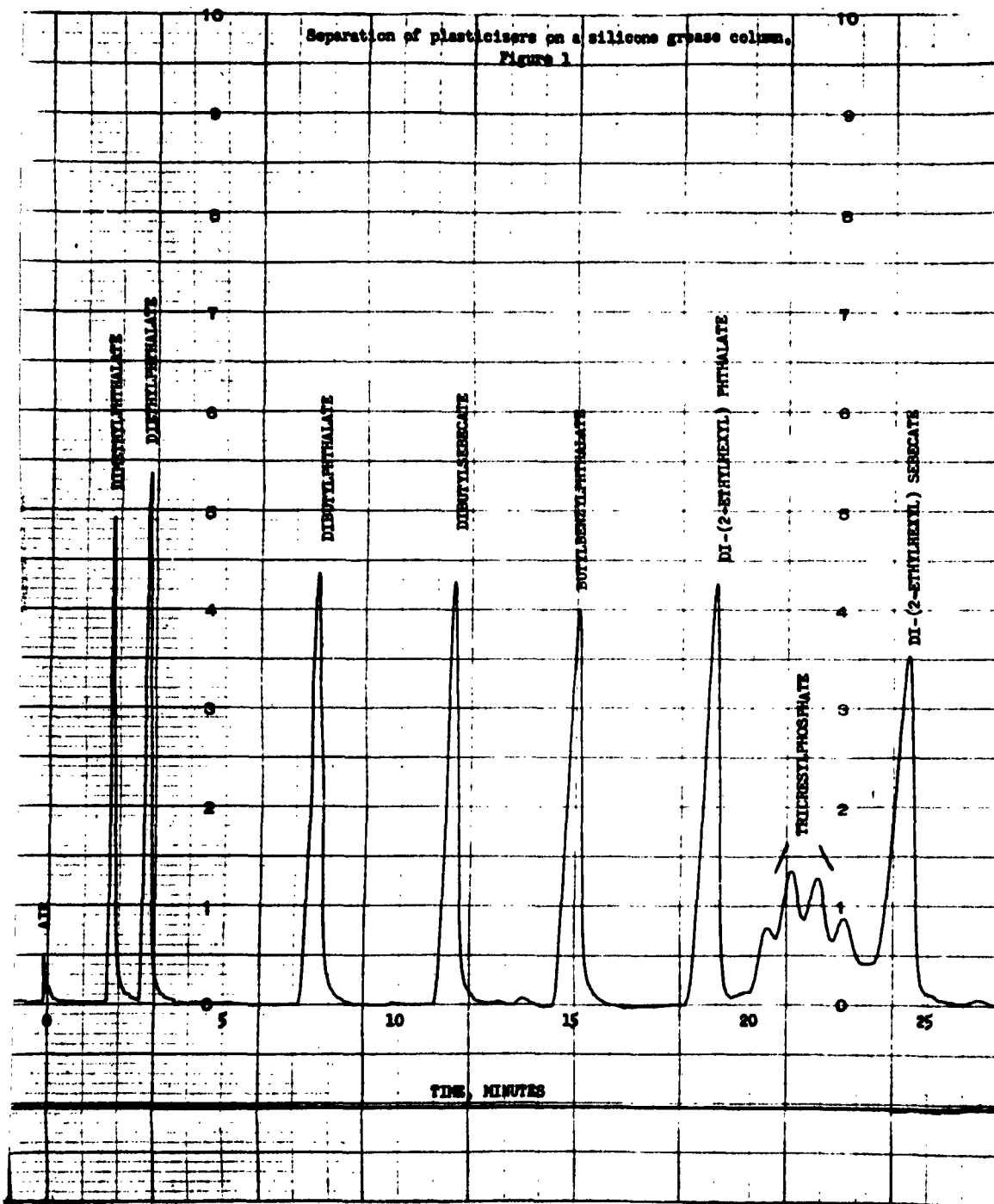
ANALYSIS OF KNOWN LACQUERS

Type of Lacquer	Plasticizer used	Present, %	Found, %
1. Nitrocellulose	Tricresyl phosphate	12.5	12.6; 12.1
2. Nitrocellulose	Di-(2-ethylhexyl) phthalate	12.0	11.7; 11.8
3. Nitrocellulose	Di-(2-ethylhexyl) phthalate	10.0	10.0; 10.3
4. Nitrocellulose	Diethyl phthalate	6.4	6.4; 6.2
	Dibutyl phthalate	6.7	6.5; 6.9
5. Nitrocellulose	Dibutyl phthalate	15.0	14.7; 14.9
6. Acrylic	Butyl benzyl phthalate	19.0	18.8; 18.9
7. Vinyl	Tricresyl phosphate	9.3	9.3; 9.3

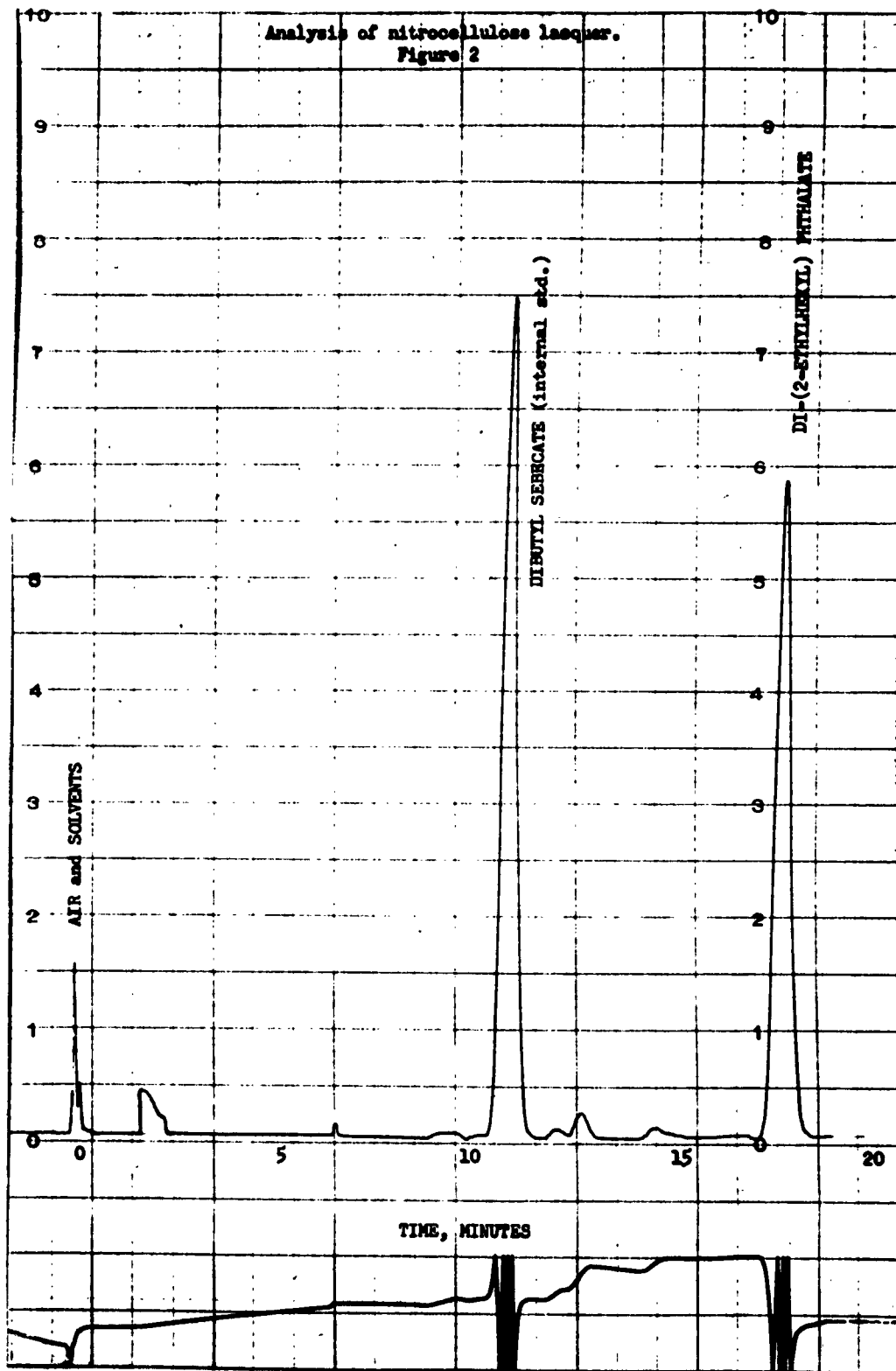
APPENDIX B

Figures

Separation of plasticizers on a silicone grease column.
Figure 1

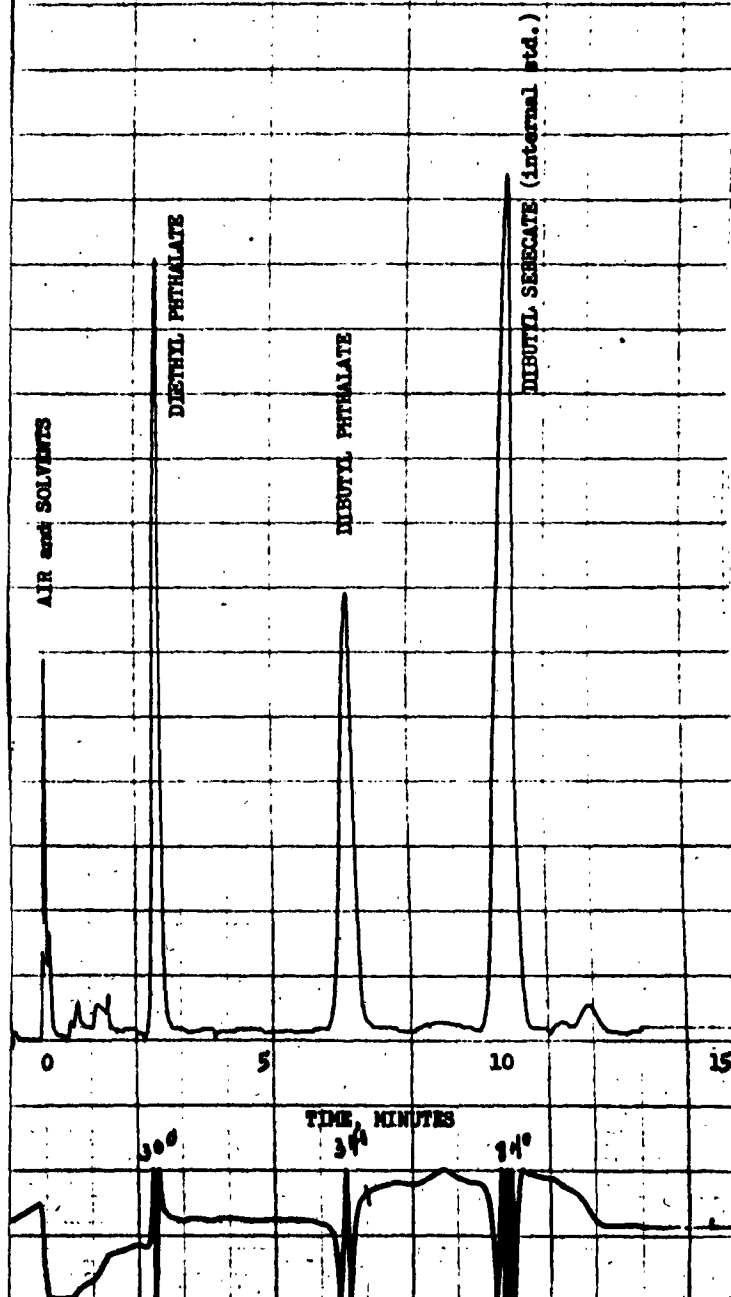


Analysis of nitrocellulose lacquer.
Figure 2

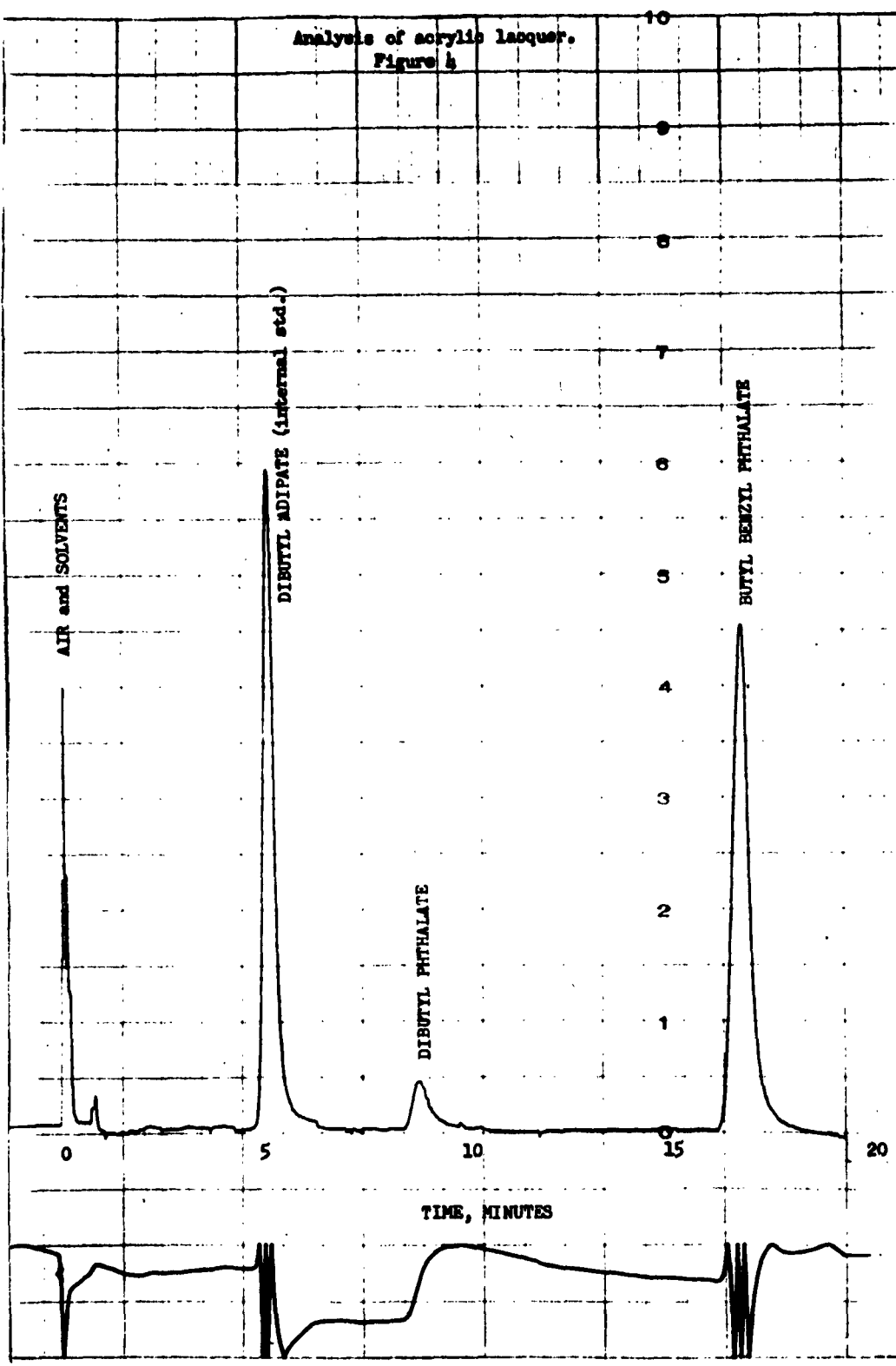


Analysis of nitrocellulose lacquer with two plasticizers.

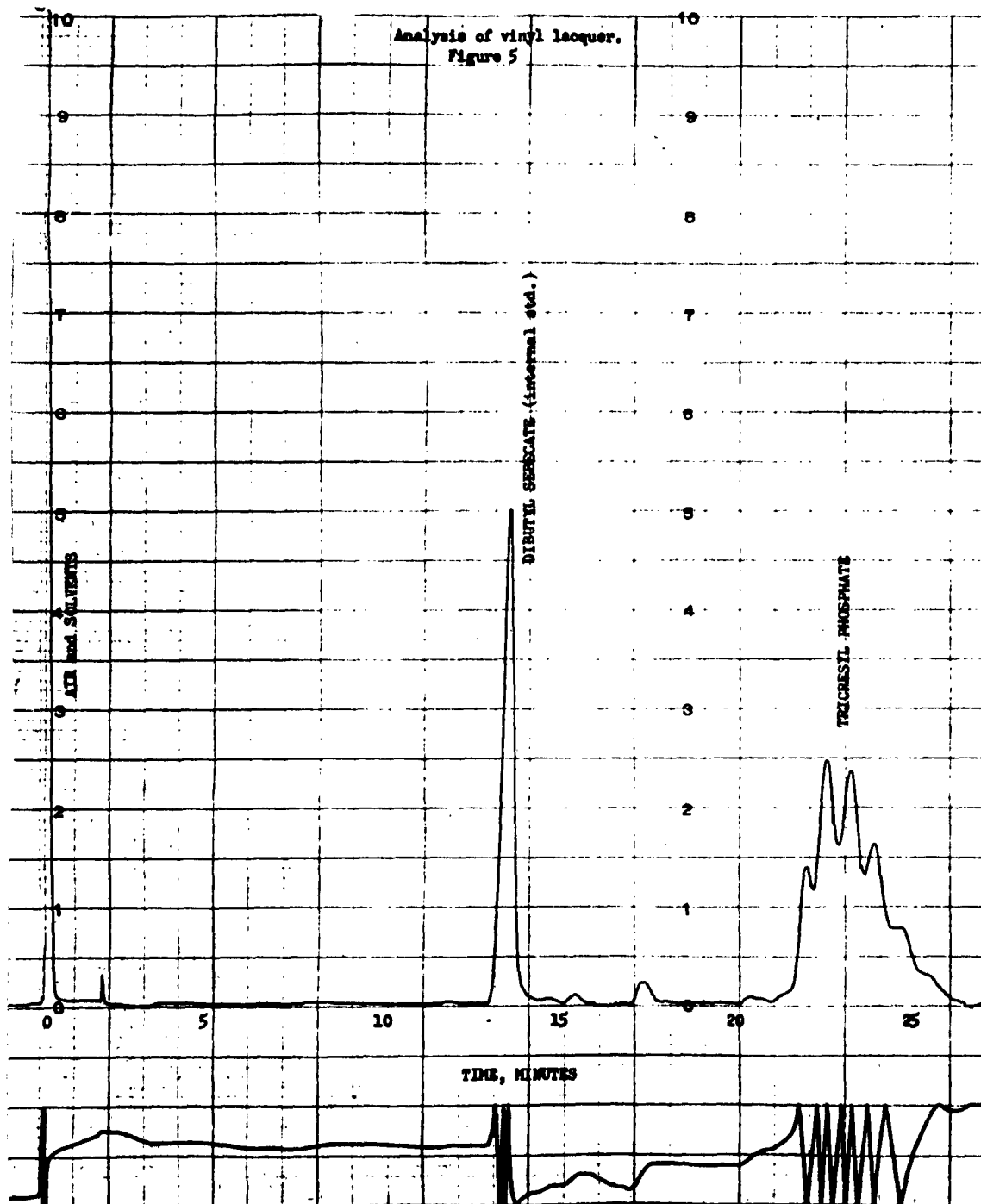
Figure 3



Analysis of acrylic lacquer.
Figure 4



Analysis of vinyl lacquer.
Figure 5



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